

# The Decay Properties of the Finite Temperature Density Matrix in Metals

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Using ordinary Fourier analysis, the asymptotic decay behavior of the density matrix  $F(\mathbf{r}, \mathbf{r}')$  is derived for the case of a metal at a finite electronic temperature. An oscillatory behavior which is damped exponentially with increasing distance between  $\mathbf{r}$  and  $\mathbf{r}'$  is found. The decay rate is not only determined by the electronic temperature, but also by the Fermi energy. The theoretical predictions are confirmed by numerical simulations.

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The decay behavior of the density matrix is a fundamental property of quantum mechanical systems since it determines the degree of locality<sup>1</sup> of all relevant quantities. Experimentally it is well known, that most quantities such as bonding properties and energies or magnetic moments depend only on an environment comprising a few nearest neighbor shells. Locality is certainly much stronger in insulators, but is also applies in metals. Recently there has also been renewed interest in these decay properties, since they determine whether and for what system size so called  $O(N)$  methods<sup>2</sup> are faster than traditional electronic structure algorithms. The decay behavior of the density matrix in insulators has been the subject of several studies. It was shown that the decay constant is related to the location of branch points of the band structure in the complex energy plane<sup>3,4</sup>. Since this is a quantity which is not accessible in ordinary electronic structure calculations, it would of course be highly desirable to relate the decay to features of the real part of the band structure. For the case of periodic solids arguments can therefore be found proposing a relation between the size of the gap and the decay behavior<sup>5-7</sup>. Based on an analysis of the expansion of the density matrix in terms of Chebychev polynomials, this was recently confirmed<sup>8</sup> for arbitrary systems.

In this paper the decay properties of the finite temperature density matrix in metals will be studied. Contrary to a widespread belief that the decay constant is given by  $\sqrt{k_B T}$  where  $k_B$  is Boltzmann's constant and  $T$  the electronic temperature, we find that the decay is as well determined by the Fermi level.

In the finite temperature formalism of Mermin<sup>9</sup> the finite temperature density matrix  $F$  is given by

$$F(\mathbf{r}, \mathbf{r}') = \sum_n \int_{BZ} d\mathbf{k} f\left(\frac{\epsilon_n(\mathbf{k}) - \mu}{k_B T}\right) \Psi_{n,\mathbf{k}}^*(\mathbf{r}) \Psi_{n,\mathbf{k}}(\mathbf{r}') \quad (1)$$

where  $\Psi_{n,\mathbf{k}}(\mathbf{r}) = u_{n,\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$  are the Bloch functions associated with the wave vector  $\mathbf{k}$  and  $n$  is the band index. The function  $f\left(\frac{\epsilon_n(\mathbf{k}) - \mu}{k_B T}\right)$  is the Fermi distribution

for the band-structure energy  $\epsilon_n(\mathbf{k})$  and for the chemical potential  $\mu$ . The integral extends over the Brillouin zone (BZ).

The cell periodic part of the Bloch functions  $u_{n,\mathbf{k}}(\mathbf{r})$  can be pulled out of the integral using the medium value theorem. Denoting the medium value by  $k_0(\mathbf{r}, \mathbf{r}')$  one obtains

$$F(\mathbf{r}, \mathbf{r}') = \sum_n u_{n,\mathbf{k}_0(\mathbf{r}, \mathbf{r}')}^*(\mathbf{r}) u_{n,\mathbf{k}_0(\mathbf{r}, \mathbf{r}')}(\mathbf{r}') \int_{BZ} d\mathbf{k} f\left(\frac{\epsilon_n(\mathbf{k}) - \mu}{k_B T}\right) e^{i\mathbf{k}(\mathbf{r} - \mathbf{r}')} \quad (2)$$

The part we have taken out is periodic in both  $\mathbf{k}$  and  $\mathbf{r}$  and bounded from above since the wavefunctions  $u_{n,\mathbf{k}}(\mathbf{r})$  are normalizable. If  $n$  refers to the lowest band the expression can also never vanish since  $u_{n,\mathbf{k}}(\mathbf{r})$  has no nodes. Hence the expression is bounded from below as well and it can therefore not influence the asymptotic behavior. In the case of higher bands the expression can in principle vanish and might lead thus a faster asymptotic decay. If the  $u_{n,\mathbf{k}}(\mathbf{r})$  has for instance an  $p_z$  like character, the cell periodic part can identically vanish for certain directions of  $\mathbf{r}$  and for certain values of  $\mathbf{r}'$ . The expression can however certainly not vanish for all values of  $\mathbf{r}$  and  $\mathbf{r}'$ . Thus the conclusion that the cell periodic part does not change the overall asymptotic behavior remains valid.

In addition we will assume that the band structure can be approximated by the free electron band structure. The decay behavior of the metallic system is thus the same as the one of jellium

$$F(\mathbf{r}, \mathbf{r}') = \int e^{i\mathbf{k}(\mathbf{r} - \mathbf{r}')} f\left(\frac{\frac{1}{2}k^2 - \mu}{T}\right) d\mathbf{k} \quad (3)$$

Using elementary calculus this three-dimensional integral can be transformed into an one-dimensional one. Using integration by parts the Fermi distribution can be replaced by its derivative  $f'$  and one obtains

$$F(s) = -\frac{2\pi}{T} \frac{1}{s} \frac{\partial}{\partial s} \frac{1}{s} \frac{\partial}{\partial s} \int_{-\infty}^{\infty} e^{iks} f'\left(\frac{\frac{1}{2}k^2 - \mu}{T}\right) dk \quad (4)$$

where  $s = |\mathbf{r} - \mathbf{r}'|$ .

To proceed further with an analytic evaluation of the resulting expression one has to approximate  $f'$  by a replacement function. The basic idea is that as the temperature tends to zero the part coming from  $f'$  becomes a delta function. So in the following steps we will replace  $f'$  by another representation of the delta function and we will use the rules which are valid for delta function for our sharply peaked finite temperature function as well even though it becomes a delta function only in the limit

of zero temperature. A good choice for the replacement function is the following

$$f'(x) \rightarrow -\frac{\sinh(ax)}{\sinh(bx)} \quad (5)$$

where  $a = \frac{\pi}{4} \tan\left(\frac{\pi}{8}\right)$  and  $b = \pi \tan\left(\frac{\pi}{8}\right)$ . The coefficients  $a$  and  $b$  were chosen such that the replacement function has the same local and global behavior as the original function. The evaluation of the remaining integral then gives

$$F(s) = \frac{4\pi c}{k_F s} \frac{\partial}{\partial s} \frac{1}{s} \frac{\partial}{\partial s} \left[ \frac{\cos(k_F s)}{1 + \sqrt{2} \cosh\left(-c \frac{k_B T}{k_F} s\right)} \right] \quad (6)$$

where  $c = 1 + \sqrt{2}$  and where  $k_F$  is the Fermi wave-vector related to the chemical potential by  $\frac{1}{2}k_F^2 = \mu$ .

So we see two prominent features in the behavior of the density matrix. It has oscillations whose wave-vector is given by the Fermi wave-vector  $k_F$  and it is decaying exponentially, since for large values of  $r$  the expression  $\left(1 + \sqrt{2} \cosh\left(-c \frac{k_B T}{k_F} r\right)\right)^{-1}$  tends to  $\exp\left(-c \frac{k_B T}{k_F} r\right)$ . Despite the approximative character of Equation 6 one obtains very good agreement in the jellium case between the exact density matrix obtained numerically and its approximation (Equation 6) over many orders of magnitude as shown in Figure 1.

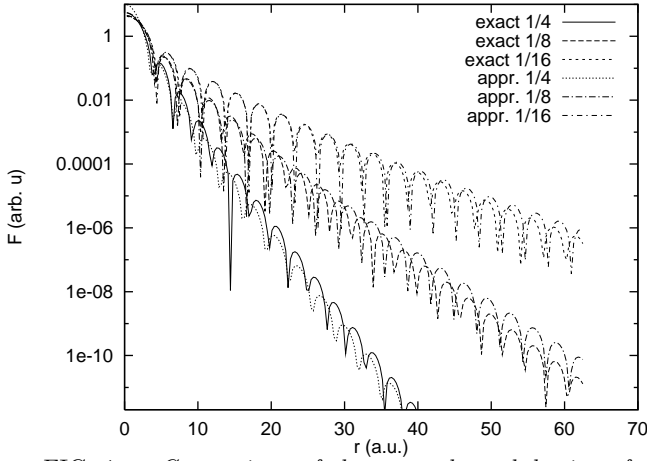


FIG. 1. Comparison of the exact decay behavior of the density matrix and its approximation of Equation 6. Three different thermal energies  $k_B T$  of 1/4, 1/8 and 1/16 are plotted for  $k_F = 1$ .

Let us note that all the approximations used in the derivation become exact as the temperature tends to zero and consequently we obtain the correct zero temperature result.

$$F(s) = -\frac{4\pi k_F}{s^2} \left( \cos(sk_F) - \frac{\sin(sk_F)}{sk_F} \right) \quad (7)$$

This confirms the well known fact that the amplitude decays algebraically in the zero temperature case. More specifically a decay proportional to  $r^{-2}$  is found.

Since the derivation was based on the assumption that the band structure is free electron like, the results may not be applicable in the case of metals which have a very complicated Fermi surface arising from a band-structure which is completely different from the free electron band structure.

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<sup>1</sup> W. Kohn, Phys. Rev. Lett. **76**, 3168 (1996)

<sup>2</sup> W. Yang, Phys. Rev. Lett. **66**, 1438 (1991) ; W. Yang and T.-S. Lee, J. Chem. Phys. Rev. B **103**, 5674 (1995) ; S. Goedecker, M. Teter, Phys. Rev. B **51**, 9455 (1995) ; A. F. Voter, J. D. Kress and R. N. Silver, Phys. Rev. B **53**, 12733 (1996) ; S. Goedecker, J. of Comp. Phys. **118**, 261 (1995) ; X.-P. Li, W. Nunes and D. Vanderbilt, Phys. Rev. B **47**, 10891 (1993) ; M. S. Daw, Phys. Rev. B **47**, 10895 (1993) **6** 9153 (1994) ; F. Mauri, G. Galli and R. Car, Phys. Rev. B **47**, 9973 (1993) ; P. Ordejon, D. Drabold, M. Grumbach and R. Martin, Phys. Rev. B **48**, 14646 (1993) ; J. Kim, F. Mauri and G. Galli, Phys. Rev. B **52**, 1640 (1995) ; A. Horsfield, A. Bratkovsky, D. Pettifor and M. Aoki, Phys. Rev. B **53**, 1656 (1996) ; E. Hernandez and M. Gillan, Phys. Rev. B **51**, 10157 (1995)

<sup>3</sup> J. des Cloizeaux Phys. Rev. **135**, A685 (1964)

<sup>4</sup> J. des Cloizeaux Phys. Rev. **135**, A698 (1964)

<sup>5</sup> W. Kohn, Phys. Rev. **115**, 809 (1959)

<sup>6</sup> W. Kohn, Phys. Rev. B **7**, 4388 (1973)

<sup>7</sup> W. Kohn, Chem. Phys. Lett. **208**, 167 (1993)

<sup>8</sup> R. Baer and M. Head-Gordon, Phys. Rev. Lett. **79**, 3962 (1997)

<sup>9</sup> N. D. Mermin, Phys. Rev. **137 A**, 1441 (1965)